DEVELOPMENT OF ON-LINE GC/MS MONITORING TECHNIQUES FOR HIGH PRESSURE FUEL CONVERSION PROCESSES

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INTRODUCTION

It is well known that on-line analytical methods offer considerable advantages over conventional off-line procedures for fuel conversion processes. Although many on-line spectroscopic detection systems for thermal process reactors have been reported [1-10], they have had only very little application to high pressure reactors [8-10]. Therefore, relatively little is known about the precise pathways and intermediate products involved in high pressure reactions. The application of real time, on-line chromatographic and/or spectroscopic techniques capable of throwing light on these processes is hampered by the high temperatures and pressures inside the reactor which complicate direct interfacing to standard analytical instruments.

As shown in previous work, thermogravimetry (TG) can provide detailed information on thermally driven conversion reactions, especially when combined with on-line detection and identification techniques such as Fourier transform infrared spectroscopy (FTIR) [1-7] and mass spectrometry (MS) [6,7]. However, high pressure TG systems have only recently become available for studying the basic pyrolysis and especially hydropyrolysis reactions involved in coal liquefaction, thus, the combined chromatographic/spectroscopic interfaces for such high pressure systems are only now producing results [11]. Other high pressure reactors of interest include those used to study the thermal processes in liquid fuels or in solvent based coal conversion. Thus there have been recent reports of on-line GC/MS monitoring of a high pressure recirculating autoclave used to study coal derived liquid model compounds [10]. Other work in our laboratory has examined the supercritical pyrolytic degradation of jet fuels with on-line GC/IR/MS [9]. Several of these systems have involved the use of a patented [12] automated vapor sampling (AVS) inlet [13] with short column or so called "transfer line" gas chromatography (TLGC) with MS [9-11] or FTIR [9].

This paper presents the experimental descriptions and results from three high pressure systems using a variety of components. The first is a high pressure TG/GC/MS system used to study coal hydropyrolysis. The other two use quartz tubing reactors to examine the liquid and gaseous products from the thermal decomposition of jet fuels.

EXPERIMENTAL

1. System I (thermogravimetry): Figure 1 shows a schematic diagram of a high pressure thermogravimetric analysis system with on-line GC/MS. The system utilizes a CAHN TG-151 high pressure thermogravimetry (TG) instrument which operates at pressures up to 1000 psi with temperatures up to 1000 C at heating rates up to 25 C/min. The MS system is a mass selective

detector (MSD, HP 5871A) with a HP 9000 computer. The TG to MS interface consists of a 1 m long 50 μm i.d. fused silica capillary, pressure reduction line for transferring vapor products at flows of 10-20 ml/min (at ambient pressure) to an automated vapor sampling (AVS) inlet developed at the University of Utah [12,13]. The AVS inlet performed pulsed sampling of the vapor product stream into a 2 m long, 150 μm i.d., 0.12 μm film thickness fused silica capillary (CP SIL-5CB, Chrompak) column directly connected to the MSD.

A 60 mg sample of coal was loaded into a specially-designed quartz crucible [11] and was placed in the high pressure TG. The TG system was purged with the reagent gases which were then set to their run flow ratio of 10:10:4 for the reagent gas, furnace flush gas and balance flush gas, respectively. The system was operated at 900 psi with H_2 as the reagent gas and He for both flush gases. The total flow rate of the gases into the TG was adjusted to 1200 ml/min at ambient pressure. The pressure reduction line and AVS were heated to 200 C to minimize condensation losses, and the TLGC column was heated to 90 C for the analysis reported here. The TG and AVS-GC/MS systems were operated by two separate computers. Detailed parameters for the reactions (including systems II and III) are listed in Table 1.

2. System II (continuous fluid flow reactor): A similar pressure reduction capillary and AVS-GC/MS system have been used for a newly developed microscale quartz tube reactor for on-line liquid product analysis as shown in Figure 2. The continuous flow reactor consists of a 300 mm long, 2 mm i.d. quartz tube in a furnace with a uniform 150 mm long heated zone, which can be heated up to 1100 C at heating rates up to 50 C/min with the temperature measured both inside and outside the quartz chamber. The sample fluid flow can be precisely controlled at 0 to 5 ml/min at pressures up to 2000 psi using an HPLC pump (Milton Roy Co.). The pressure reduction line is a 1 m long, 25 μm i.d. fused silica capillary with a volume flow of approximately 2 μl/min. The filter frits and capillary are attached to the reactor to minimize the high pressure dead volume and minimally disturb the reaction process. The AVS-GC system used a 2 m long, 150 μm i.d. fused silica capillary column (CP SIL-5CB) which could be temperature programmed from 30 to 280 C at heating rates up to 150 C/min. The GC column was directly coupled to a modified Ion Trap Mass Spectrometer (ITMS, Finnigan MAT) with tandem MS capabilities and electron ionization (EI) as well as chemical ionization (CI) options.

The sample solution was continuously pumped from a glass reservoir into the reactor at the chosen flow rate by the high pressure liquid pump. For experiments on the effect of dissolved oxygen during the thermal degradation, pure oxygen (or air) was bubbled via a 10 μm porous filter in the sample reservoir, otherwise, pure nitrogen was bubbled to exclude oxygen. For some tests, a metal foil was inserted into the reactor from one end to serve as a catalyst. The reactor was pressurized to 1500 psi by adjusting the flow-splitting needle valve. The preheater was set at 250 C (590 F). Ten minutes after the reaction temperature was reached, the first AVS sample was taken and the GC temperature was programmed with an initial hold at 30 C for 5 min and then linearly heated to 250 C in 20 min for each vapor sample. The results of four or more repetitive samples were continuously recorded by a PC computer.

3. System III (continuous fluid flow reactor with product phase separation): Figure 3 shows the continuous flow reactor with on-line AVS-GC/MS for gaseous product analysis. Components which differ from system II include: a backpressure regulator (Grove Valve & Regulator Co. model 91W) which maintains the pressure in the reactor while conducting a mixed phase mass flow of 0 to 10 mg/min at ambient pressure; a gas-liquid separating device for the products; and

a Mettler AE 240 electronic micro balance system interfaced to a PC computer with ~ 40 g of weighing capacity and 0.1 mg accuracy. The AVS inlet was used on a Hewlett Packard 5890II Gas Chromatography system with a 10 m long, 530 μm i.d. porous layer fused silica capillary column (GS-Q, J & W Scientific). The outlet of the column was connected via an open split interface and a 0.5 m long x 100 μm i.d. capillary to an MSD (HP 5971A) with a 1993 HP Chemstation PC software system, which can scan from m/z 1.2 to monitor H_2.

In order to focus our analytical attention on the smaller hydrocarbon products, eg. C_1 through C_3, the reactor system was modified from that of Fig. 2 to that shown in Fig. 3. The experimental procedure was similar to system II except that the reactor's pressure was controlled by adjusting the controlling gas pressure to the backpressure regulator valve, and the continuous recording of liquid product weight. A one hour run was used for weight analysis while ten repetitive samples were taken for MS. The use of the MSD with its updated software enabled scanning a mass range to include hydrogen although its detection is not reported here.

RESULTS AND DISCUSSION

System I: Fig. 4 shows high pressure TG/GC/MS data from the hydropyrolysis of a Blind Canyon, Utah coal in H_2 at 900 psi. Fig 4(a) shows the thermogravimetry (TG) and first derivative of the TG (DTG) curves for the temperature range of 400 to 600 C at 10 C/min with a 5 min hold at the final temperature. The major weight loss process centered at 450-460 C to the main coal pyrolysis step in helium (He). The second DTG peak near 570 C was not obtained in runs in He (see related work in ref. 11). Fig. 4(b) shows a corresponding ion chromatogram for a phenolic fragment ion (m/z 107) which indicates that alkylphenols are even greater abundance in the higher temperature process than in the main pyrolysis. The same selected ion is shown with an expanded time scale in Fig 4(c) to demonstrate the amount of isomer and homolog separation available on the short GC column; the o-cresol peak is partially resolved from the m- and p-isomers, and the dimethylphenols are largely separated from the ethylphenols.

System II: The total ion chromatograms (TICs) of a JP-7 jet fuel sample subjected at 1500 psi to different temperatures with a mean residence time of 2.0 min are presented in Fig. 5 for the 20 min temperature program runs. Since the unreacted jet fuel is composed of saturated straight chain and cyclic hydrocarbons, with from nine to sixteen carbons and traces of aromatics, its supercritical point is estimated to be at a temperature of 400 C (750 F) and a pressure of 250 psi. Under supercritical conditions the thermal decomposition products are dominated by short chain components. The results in Fig. 5 show that below the supercritical condition (77 F), no decomposition products were detected, while at higher temperatures (800 and 900 F), significant levels of C_2 - C_7 products were obtained and the quantity increased with the reaction temperature. To determine the influence of oxygen and catalysts during the thermal decomposition, oxygen, metal foil (~100 mm^2) and organic metal were added in separate experiments. Fig. 6 shows the various effects of oxygen, metal Cu and 1 ppm of Cu(II) 2,4-pentanedionate on the decomposition of JP-8 (all at the single temperature of 900 F). As seen in Fig. 6 the addition of oxygen and catalysts significantly increased the decomposition products (C_2 - C_7). Although in all of these preliminary experiments the objective was to demonstrate steady state reaction conditions, it can be seen that the complete fuel could be monitored for compositional changes from C_2 to C_{17} with cycle times of 25 min or less.

System III: Fig. 7 shows the weights of the total liquid materials (sample plus liquid products) versus reaction time for JP-7 jet fuel decompositions (a) at different reaction temperatures and (b) its gas conversion with and without addition of methycyclohexane vs reaction temperature. Because methycyclohexane is a hydrogen donor, its addition to the JP-7 jet fuel produced the highest gas conversion. Fig. 8(a) illustrates the relative amount of the low molecular weight products such as methane, ethylene, ethane, propylene, and propane under the supercritical conditions. Fig 8(b) shows analysis of standard mixtures consisting of 25% methane, 25% ethylene, 25% propylene and 25% butylene.

CONCLUSIONS

Fast, repetitive "transfer line" GC/MS (TLGC/MS) analysis of products from high pressure reactors by means of a heated capillary pressure reduction line is feasible provided compounds of interest are sufficiently volatile and stable. TLGC/MS analysis can be performed regardless of whether reactor contents are in the vapor, liquid or supercritical fluid phase or their mixtures. However, careful removal of particulate matter from the product stream is required to prevent plugging of the pressure reduction line.

Use of quartz tubing reactors reduced the possibility of catalytic effects from the walls of the reaction vessel and made it easier to visually observe the reaction processes and residue formation in the reaction chamber compared to other systems (such as stainless steel tubing reactors or autoclaves). The high pressure TG/AVS-GC/MS system reliably handled solid samples in reactive atmospheres with simultaneous sample weight and evolved gas product GC/MS monitoring. The newly developed, on-line quartz-reactor AVS-GC/MS systems for high pressure reactions continuously handled gaseous, liquid, and supercritical liquid samples reliably. The system II sampling interface was efficient for high molecular weight (liquid and supercritical liquid) product analysis. The system III interface was sufficient for low molecular weight (gases) product analysis and was demonstrated here with continuous monitoring of the sample weight conversion. Therefore, the newly developed systems represent a significant improvement over conventional off-line methods and should facilitate elucidation of the mechanisms and kinetics of fuel conversion processes.

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TABLE 1: EXPERIMENTAL CONDITIONS

Conditions	System I	System II	System III
1. Sample	Blind Canyon coal in hydrogen	JP-7 & JP-8 jet fuel	JP-7 jet fuel
2. Reactor	high pressure thermobalance CAHN model TG-151 temp: ambient to 1000 C	quartz tube flow through reactor with catalytic inserts; temp: ambient to 1100 C; residence time:1 sec to 5 min	quartz tube flow through reactor with catalytic inserts; (with a micro-balance)
3. Pressure reduction line	900 psi →ambient 1 m x 0.050 mm fused silica cap.	1500 psi →ambient 1 m x 0.025 mm fused silica cap.	1000 psi →ambient backpressure regulator
4. Vapor sampling inlet	120 C; pulse: 500 ms at 75 sec intervals	250 C; pulse: 800 ms at 25 min intervals	40 C; pulse: 400 ms at 2 min intervals
5. Transfer line GC column	2 m x 0.150 mm Me-silicone 0.12 μm 90 C isothermal	2 m x 0.150 mm Me-silicone 0.12 μm 30-200 @ 15 C/min	10 m x 0.530 mm Porous large cap. 40 C isothermal
6. Detector	quadrupole mass spectrometer- model HP 5971 (Hewlett-Packard) with a HP 9000 computer	Miniaturized Ion Trap Mass Spectrometer (Finnigan-MAT) with a PC computer	quadrupole mass spectrometer- model HP 5971 (Hewlett-Packard) with a PC computer
7. Mass range	m/z 10 ~ 300	m/z 10 ~ 500	m/z 1.2 ~ 80

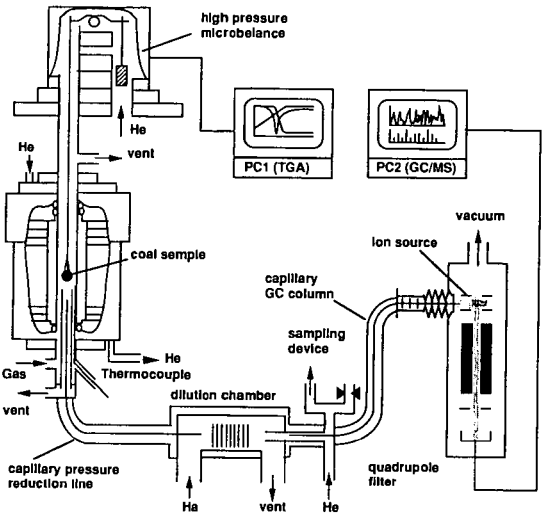

Figure 1. High pressure TG/GC/MS system (system I)

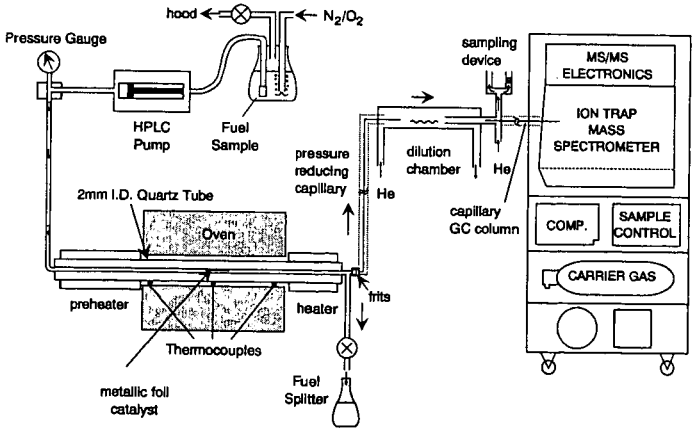

Figure 2. On-line GC/MS monitoring of high pressure fluid, flow-through reactor (system II)

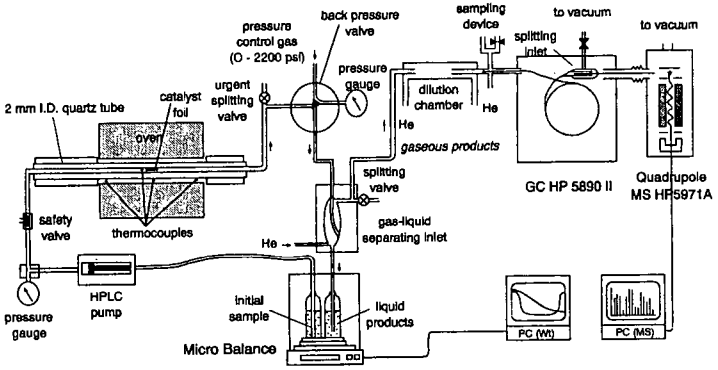

Figure 3. On-line GC/MS monitoring of high pressure fluid, flow-through reactor with product phase separation (system III).

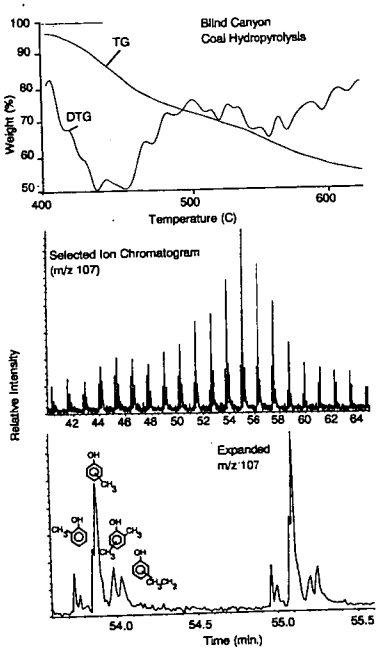

Figure 4. Partial TG/GC/MS data from the analysis of the Blind Canyon, Utah coal in H_2 (900 psi, 10 °C/min) showing the detailed monitoring of alkylphenols in the evolved gases.

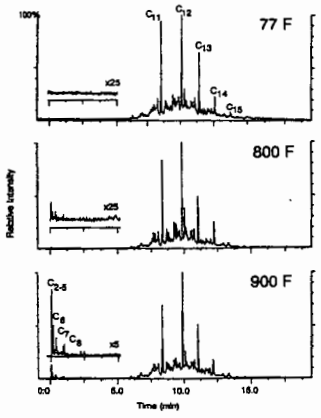

Figure 5. Effect of reaction temperature on the thermal decomposition of JP-7 jet fuel under supercritical conditions (1500 psi) in a 2 mm i.d. quartz tube flow-through reactor, system II (residence time 2.0 min).

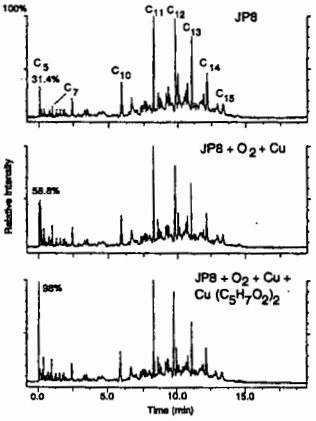

Figure 6. Effect of catalysts on the thermal decomposition of JP-8 jet fuel in system II under supercritical conditions (1500 psi, 900 F, 2.0 min residence time).

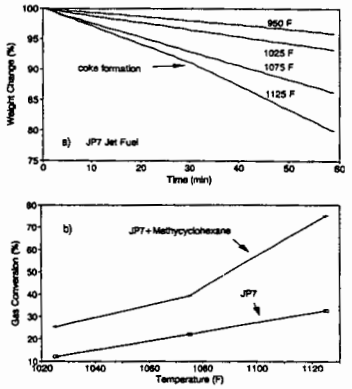

Figure 7. Effect of reaction temperature on (a) the weight change of liquid sample plus liquid product and on (b) the gas conversion of supercritical thermal decomposition of JP-7 jet fuel (1000 psi, < 1.5 min residence time).

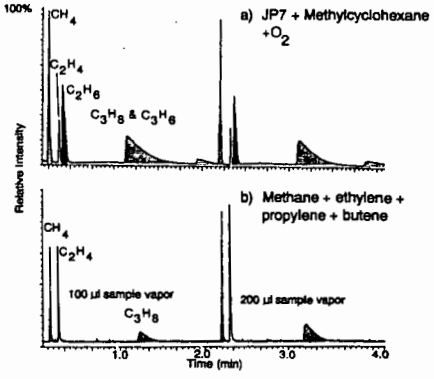

Figure 8. GC/MS profiles of (a) gaseous products of supercritical thermal decomposition of JP-7 jet fuel (1000 psi, 1000F, < 1.5 min residence time) and (b) standard compounds (25% for each of methane, ethylene, propylene and butene).